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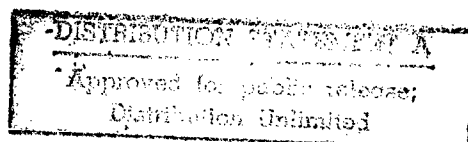
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IN CARBON MONOXIDE BY THE THERMODIFFUSION METHOD

- USSR -

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THE CONCENTRATION OF ISOTOPES C^{13} AND O^{18} IN CARBON MONOXIDE BY THE THERMO-DIFFUSION METHOD

Following is a translation of an article
G. M. Panchenkov and V. D. Moiseyev written
in Zhurnal Fizicheskoy Khimiyi (Journal of
Physical Chemistry), Vol. XXX, No.7, Moscow,
1956, pages 1662-67.

As shown by theoretical computation, the single-stage factor of the separation of isotopes of carbon by means of thermo-diffusion is higher for carbon monoxide than for carbon dioxide. Therefore, in spite of certain inconveniences in work with carbon monoxide because of its toxicity, it is advantageous to produce the concentration of the isotope C^{13} using carbon monoxide as fissionable gas.

Besides, carbon monoxide, unlike methane for which the single-stage separation factor is still higher, is more stable thermally and can easily be obtained in a pure state, which excludes the negative effect of impurities on the separation process. There is only one written work on the separation of the isotopes of carbon by means of the thermo-diffusion of carbon monoxide [1], which was carried out under conditions different from those examined below.

Experimental Part

The thermal diffusion column used by us and made entirely of molybdenum glass is shown in Fig. 1. It represents a vertical tube (1) of 0.40 cm inside radius. It is cooled on the outside by running water at a temperature of 291 K. A molybdenum electrode (2) is sealed into the tube's top, from which is suspended a platinum wire (3) 287 cm long and of 0.015 cm rad. Little glass stars soldered to the wire center it along the axis of the column. To the lower end of the wire a weight (4) is attached which is made of a glass tube filled with mercury, and sealed at the ends. A heavy molybdenum wire runs along the axis of this tube; the lower end of the wire is immersed into mercury (5) and a molybdenum electrode (6) is inserted into the tube from the outside.

The platinum wire (3) is heated by a stabilized alternating current, the voltage of which is regulated by an auto transformer. The temperature of the wire is determined by the change of its resistance.

The upper end of the thermal diffusion column is connected by means of a ring shaped convection tube, heated by a spiral (7) to 150°C., with the "infinite" reservoir (8) of abt 2.5 liter capacity. The lower end of the column is connected in the same manner with a changeable reservoir (9) of 60 ml capacity. This reservoir can be detached from the column and the gas it contains analyzed or used for other purposes.

The upper convection tube is connected with a mercury manometer (10). The lower convection tube, close by the winding of the electric furnace (11), has a tubulus connected with the initial vacuum oil pump, the system of gas generation and purification (not shown in the Figure), and the ampoules (12) for gas sampling. The ampoules are removed simply by unsoldering.

The ampoule has a volume of 5 ml. Its upper end is closed by a sealed capillary protected by a glass tube. This tube can be soldered to the instrument needed, and the capillary broken by an iron weight and magnet; this releases the gas contained in the ampoule into the testing device.

Carbon monoxide for filling the column was produced in a glass apparatus evacuated by an initial vacuum pump, by adding formic acid (drop by drop) to concentrated sulfuric acid heated to 100-110°C. Carbon monoxide was purified by consecutive passings through solutions of potassium permanganate, potassium hydroxide, and concentrated sulfuric acid, after which it entered into the column, evacuated to 0.01 - 0.001 mm mercury. The column and all the connections were previously washed out repeatedly with a flow of carbon monoxide. According to the data of the mass-spectrometer analysis, the samples of carbon monoxide from our column contained practically no air.

Each experiment began with filling up the column to the pressure desired. Then, its platinum wire was heated and, in due course, the gas samples were removed from the lower part of the column into the ampullas. By the end of the experiment, a gas sample was produced in reservoir (9) and the column was evacuated. The experiment was repeated after a spare reservoir (9) had been attached to the column.

Samples of carbon monoxide taken from the column were analyzed by the mass-spectrometer. Since the rest-peaks of masses 12 and 13 were too high and too unstable, the measurement dealt with the ratio of the height of the peak $C^{12}O^{16}$ (with mass 28) to the summary height of the peaks $C^{13}O^{17}$ and $C^{13}O^{16}$ (with mass 29). The heights of the corresponding rest-peaks were measured before and after the introduction of the sample of carbon monoxide into the mass-spectrometer, and the average heights of these peaks, amounting normally to 2-3 percent of the peak-heights of the sample, were subtracted from the latter. The ratio C^{12}/C^{13} was computed - after accounting for O^{17} * under the assumption that due to the identical molecular weights of CO and $C^{13}O$, the ratio of the concentrations of these molecules is the same in the gas sample from the lower part of the column as in the initial gas. The error in the determination of the content of isotope C^{13} amounted to 0.3-0.4 percent of its content in the sample.

We performed six experiments with the thermal diffusion column.

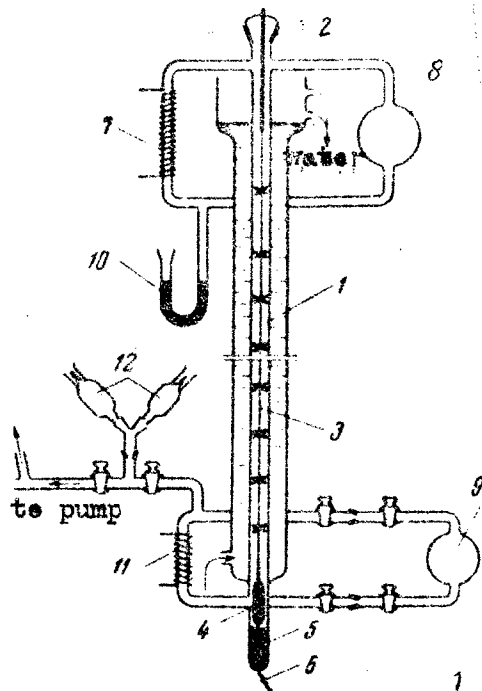


Fig. 1. Thermal diffusion column.

*It was assumed that the ratio O^{16}/O^{17} in carbon monoxide was 9978 /2/.

In the first five experiments, the pressure of carbon monoxide in the column varied under a constant temperature of the platinum wire equaling 730°C. The sixth experiment was performed at practically the same pressure, (750 mm of mercury column) as experiment 1, but the temperature of the wire had been raised to 860°C.

In the fourth experiment, the ratio of the heights of the peaks of masses 28 and 30 was also measured which, with the necessary reactions, gives the ratio O^{16}/O^{18} in the gas sample.

The following table presents the results of our experiments. In it:

$$q = \frac{C^{13}/C^{12} \text{ (bottom)}}{C^{13}/C^{12} \text{ (top)}}$$

is the separation factor of the carbon isotopes in our column;

$$q' = \frac{O^{18}/O^{16} \text{ (bottom)}}{O^{18}/O^{16} \text{ (top)}}$$

is the factor of separation of isotopes O^{16} and O^{18} (from experiment 4).

Expt. No.	pressure mm. hg.	t hours	q	q'
1	751	5.25 11.137	1.20:1.52 2.11:2.13	—
2	675	48.72 90.120	1.94:2.17 2.26:2.28	—
3	600	40.46 89.110	1.76:1.89 2.20:2.23	—
4	400	12.5.39.5 96.154	1.25:1.44 1.64:1.70	1.70:1.99 2.34:2.44
5	200	10.112	1.33:1.69	—
6	750	24.136	1.74:2.16	—

Fig. 2 represents the graphs plotted from the data of the table. The equilibrium was reached in effect in about 120 hours at all pressures.

Graph 5 seems to indicate that the speed of the equilibrium increases with the decrease in pressure, but this graph has too few points and such a conclusion needs verification. At 750 mm of the mercury column, a rise in tempera-

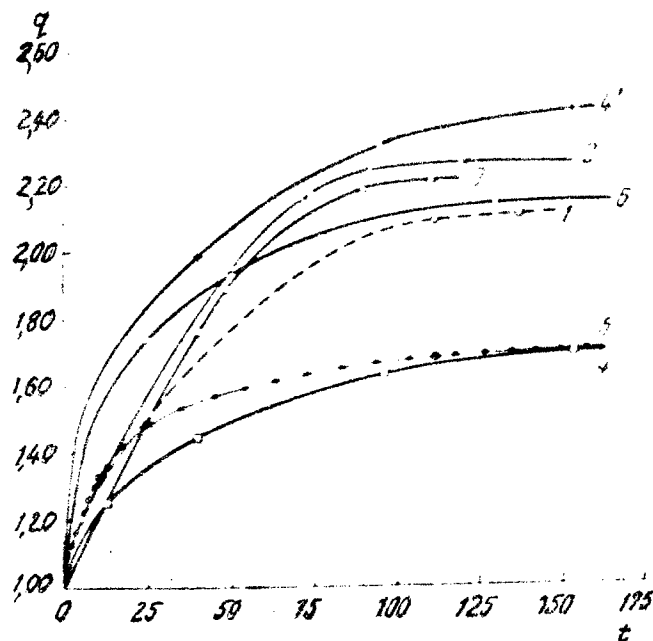


Fig. 2. Dependence of the factor of separation on time. Graphs' numbers correspond to the numbers of the experiments.

ture to 130°C. somewhat increased the separation and the speed of reaching the equilibrium (graphs 1 and 6). The maximum factor of separation depending on pressure is near 675 mm of the mercury column and is rather sharply expressed (Fig. 3).

At 400 mm of the mercury column, the separation factor of isotopes of oxygen q' is about 1.6 times greater than the one of isotopes of carbon q , which means that the isotope of oxygen O^{18} can be effectively concentrated by thermo-diffusion in carbon monoxide.

Since the physical constants of carbon monoxide are well known, the factors in the equation of transfer can be easily computed, using the widely accepted theory of thermal diffusion column of Jones and Ferry and thus the total separation factor at the point of equilibrium will be found.

This computation which uses the data of experiment 2 indicates that q_e equals 3.78, while the experiment gives the value of q_e as 2.28. The discrepancy can be explained by the parasitic convectional intermixing arising from the asymmetry of the thermal diffusion column, and the minimizing

of the separation.

According to the same theory [3], the relaxation period t_r for a column with a closed positive end and an infinite reservoir on the negative end, is defined by the following expression:

$$t_r = \frac{m}{H} \left(\frac{e^{2AL} - 1}{2AL} - 1 \right), \quad (1)$$

where m is the mass of gas in the column. Since the volume of the column equals 145 ml (without the reservoirs), its mass equals $15.12 \cdot 10^{-2}$ grams; $e^{2AL} = Q_e = 2.28$, and H in our case as is shown by computation is $9.9372 \cdot 10^{-7}$. Thus, substituting these values into the expression (1), we find that $t_r = 23.35$ hours.

According to the same theory [3], in the case of a column with an infinite reservoir at the negative end, and a large (i.e., the volume of which is much larger than the one of the column) reservoir at the positive end, the relaxation period during the concentration process of an isotope with a relative concentration of less than 1 is expressed as follows:

$$t_{r \text{ res}} = \frac{m}{H} (e^{2AL} - 1). \quad (2)$$

In our case, the volume of the positive reservoir is 60 ml.; consequently, m equals $6.17 = 6.17 \cdot 10^{-2}$ gram, $e^{2AL} = Q_e = 2.28$; $t_{r \text{ res}} = 22.08$ hours.

The expression (2) has been developed on the assumption that the time of relaxation is determined almost exclusively by the transfer of the isotope into the positive reservoir. In our case, the volume of the latter is comparable to that of the column. Such a case has not been examined by means of the theory [3].

It is obvious that the time for our column with the reservoirs must be greater than 23.35 hours but less than $23.35 + 22.08 = 45.43$ hours. The correctness of this reasoning is corroborated by experiment. In Figure 4, graph 1 is plotted from experiment data of experiment 2; graph 2 -- according to theory [3] and the equation

$$q - 1 = (q_e - 1)(1 - e^{-t/t_r}). \quad (3)$$

provided that the equilibrium values are for the separation factor $Q_e = 2.28$ and $t_r = 23.35$; graph 3 is plotted according to the same formula (3) but $Q_e = 2.28$ and $t_r = 45.43$. It is evident that $23.35 < t_r < 45.43$. The experimental relaxation

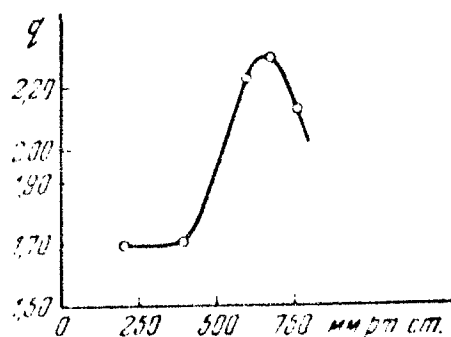


Fig. 3. Dependence of the factor of separation on the pressure in the column at 730°C.

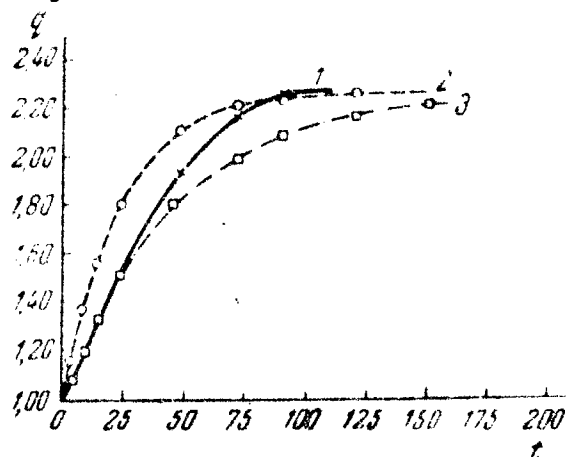


Fig. 4. Theoretical and experimental graphs of the dependence of the factor of separation on time; 1 - 1) experimental graph; 2) for $t_r = 23.35$ h.; 3) for $t_r = 45.43$ h.

time $t_{r \text{ exp}}$ could have been computed more precisely from the points of experiment 2 by the method of the least squares.

It follows that a thermodiffusion column like ours can produce an amount of concentrate of isotope of Cl^{13} , sufficient for laboratory work. Fig. 4 shows that a run of 48 hours might produce 60-80 ml of gas at 675 mm. hg., i.e., 62-73 mg of carbon monoxide with a concentration of the isotope of Cl^{13} (corresponding to the separation factor of 1.94) equaling 2.123 percent. The ratio $\text{Cl}^{12}/\text{Cl}^{13} = 46.1$.

The spectrometric error in the determination of the content of isotopes of carbon Cl^{13} usually less than 0.5 percent of the concentrations of the isotope being measured (in our case it amounted to 0.3 - 0.4 percent). This means

This means that, proceeding from an error of 0.5 percent and using as a tagged atom a sample containing $\text{Cl}^{35} = 2.123$ percent, the maximum permissible dilution will equal about $1/200$. It is evident that such a concentration is suitable for many purposes.

This Cl^{35} enriched carbon monoxide sample can be easily oxydized into carbon dioxide. We have oxydized carbon monoxide with iodine pentoxide in a glass apparatus shown in Fig. 5.

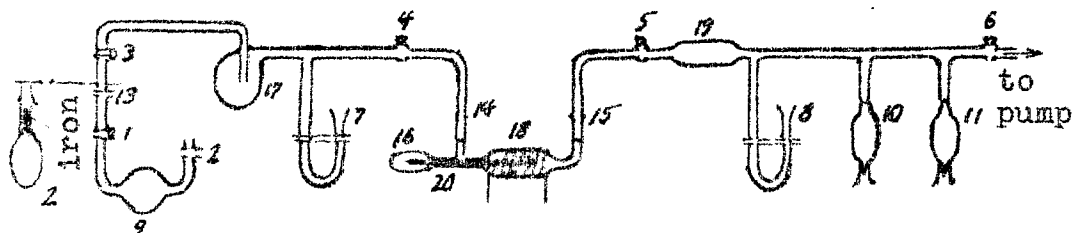


Fig. 5. Apparatus for the oxidation of carbon monoxide to dioxide: 1-6, vacuum stopcocks; 7-8, mercury manometers; 9, reservoir with carbon monoxide; 10-11, ampullas; 12, ampullas with carbon monoxide; 13-16, ground connections; 17, trap; 18, furnace with iodine pentoxide; 19, tube with freshly reduced copper spirals for trapping iodine vapors; 20, thermometer.

Spirals of fine copper wire were deoxidized by heating in a gas flame and cooled in methyl alcohol, then rapidly dried.

Iodine pentoxide was prepared from commercial iodic by heating it for 12 hours at $200-300^{\circ}\text{C}$, and a subsequent heating of the final product obtained in a vacuum at 180°C .

The process of oxidizing carbon monoxide in our apparatus was carried out as follows: all the stopcocks were opened and the apparatus evacuated to $0.01 - 0.001$ mm of mercury; then, stopcocks 4 and 6 were closed and stopcock 1 was opened, and the gas entered into the left part of the apparatus. Then, Dewar flasks with liquid nitrogen were placed under ampullas 10 and 11, and furnace 18 brought up to 120°C . Stopcock 4 was opened cautiously and the flow of carbon monoxide was allowed to pass through furnace 18, its speed being regulated so that manometer 7 would show a drop in pressure of 10 mm per minute. After some time, manometers 7 and 8 began to indicate the absence of gas in the apparatus (visible pressure less than 1 mm). Then ampullas 10 and 11 with their charge of solid carbon dioxide were evacuated and unsoldered. The mass spectrometer showed a very high purity of carbon dioxide obtained.

The method of oxidizing small samples of carbon monox-

xide into carbon dioxide here described is simple and most convenient.

Conclusions

1. The process of the concentration of isotopes of carbon C^{13} and oxygen O^{18} in carbon monoxide by the thermodiffusion method was examined.

2. The validity of the theory of the thermodiffusion column for the purpose of semiquantitative prediction of the results of the work of the apparatus with prescribed parameters was confirmed.

3. A convenient method of oxidizing small samples of carbon monoxide into carbon dioxide was developed.

Submitted, 31 December 1955.

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